VI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF CHROMIC SUPERFLUORIDE ON BENZOIC ACID.

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As the chromic superfluoride is instantly decomposed by water with the formation of chromic anhydride and hydrofluoric acid, we undertook the experiments described in the following paper in the hope that organic compounds containing hydroxyl would act in a similar way; and since Mallet's* determination of the vapor-density of hydrofluoric acid obliges us to assign it the formula H_2F_2, that thus we might obtain organic substances, in which the oxygen of the hydroxyl was replaced by two atoms of fluorine, as in fluosilicic acid. This hope has not been realized in the case of benzoic acid, with which we began our experiments, as the chromic superfluoride left the hydroxyl entirely unaltered; but, on the other hand, it has led us to a very interesting result, as the products of the reaction were chromic fluoride (Cr_2F_6) and a difluorbenzoic acid, and therefore we have achieved for the first time, so far as we can find, the direct substitution of the hydrogen in an organic substance by fluorine. Preliminary experiments with acetic acid and benzol seem to show that the reaction is a general one,—in both cases the chromic superfluoride was reduced to a lower fluoride of chromium,—and there is good promise, therefore, that it will prove of service in adding new members to the class of fluorine organic compounds, as yet so meagrely represented.

We have not made a complete study of the difluorbenzoic acid, but have contented ourselves with doing enough to characterize it thoroughly, as we are anxious to avoid any interference with Paterno, who has already begun the investigation of organic bodies in which

* Am. Chem. J., iii. 189.

hydrogen is replaced by fluorine. Nor do we intend to continue our experiments on acetic acid and benzol, as Paterno has announced that he is at work on the fluorine derivatives of both these substances. We wish, however, to reserve for our future study the action of chromic superfluoride on all other organic substances.

The remainder of the paper consists of the detailed account of our experimental work.

Action of Chromic Superfluoride on Benzoic Acid.

The chromic superfluoride was made by the action of 180 gr. of fuming sulphuric acid on 60 gr. of potassic dichromate and 100 gr. of calcic fluoride, both of which must be perfectly dry. If the fuming sulphuric acid is very strong, it should be diluted with ordinary strong sulphuric acid, as, if this precaution is neglected, the action is so violent that it cannot be controlled, a large amount of the superfluoride is wasted, and in extreme cases the cover may be blown off the lead retort. The lead retort used was of the cylindrical form figured in most text-books for making the aqueous solution of hydrofluoric acid; the fuming sulphuric acid was first introduced, the fluor-spar and potassic dichromate previously thoroughly mixed were then added, and stirred in with an iron rod, the cover put on, and the reaction started by a gentle heat. As soon as faint white fumes appear at the exit tube, the lamp should be removed, and, after the first violent evolution of gas has slackened, the action can be made to proceed smoothly by a gentle heat, although it is hard to avoid occasional rushes of gas. It is hardly necessary to say that the work should be carried on under a good hood, and the hands protected by india-rubber gloves. After the process is finished, the retort should be emptied before it has become cold, as after the residue has hardened its removal is both difficult and tedious.

The chromic superfluoride obtained in this way is not free from hydrofluoric acid, to judge from the white fumes which were observed mixed with the dark red heavy vapor; but it was pure enough for our purpose, and was allowed to act directly on the solid benzoic acid, which was spread in a layer rather less than a centimeter thick over the bottom of a platinum dish, or on its cover; for this purpose the lead pipe, which formed the exit tube of the retort, was brought down so that it nearly touched the surface of the acid. Absolute contact must be avoided, as in this case the tube soon becomes stopped up with the fused product. With a rapid stream of the superfluoride the action

is vigorous, the benzoic acid fusing and forming a black crust, which was made to spread over the whole surface by moving the dish when necessary; the crust was then removed,* and the same action repeated with fresh benzoic acid, until all the superfluoride was exhausted. In this way 180 gr. of the crusts could be obtained in a single operation. If the stream of superfluoride was not rapid, the benzoic acid was apt to become covered with chromic anhydride, probably from a trace of moisture in the acid, and this not infrequently gave rise to unimportant deflagrations; but the amount of chromic anhydride formed even by this secondary reaction is very small, almost the whole of the chromic superfluoride being converted directly into the green chromic fluoride Cr_2F_6.

To obtain the difluorbenzoic acid from the crude product it was dissolved in a strong solution of sodic carbonate, and, after the chromic hydrate had been removed by filtration, fractionally precipitated with hydrochloric acid, the liquid being boiled with the separated benzoic acid after each precipitation. We found it wisest to divide the whole into two about equal fractions at first, and then to fraction the least acid portion again, when all the difluorbenzoïc acid collected in the least acid fraction, which should be made very small; this was then boiled with water, and the residue purified by recrystallization from boiling benzol and sublimation. The yield of difluorbenzoic acid is only 1.5 per cent of the benzoic acid used.

Having obtained the difluorbenzoic acid, we next tried to detect the presence of monofluorbenzoic acid, and for this purpose examined the acid contained in the hot aqueous filtrate from boiling the difluor acid with water, and also the fraction immediately preceding the least acid one. As the metafluorbenzoic acid melts at 123°–124° according to Paterno and Oliveri,† the melting-point was of no assistance to us, and we have accordingly made a number of analyses of the barium salts of these fractions, both before and after a repetition of the fractional saturation, which have given results varying from 35.81 to 35.99 per cent of barium; baric benzoate contains 36.15 per cent, baric fluorbenzoate 33.01 per cent.‡ We also thought it might be contained in a mixture of acids, obtained by boiling the crude product with insufficient water, melting sometimes as low as 102°; but this on fractional neutralization

* We think it right to mention that both of us were poisoned, one severely, by the crude product, which was spilt on our clothes in removing the crusts from the platinum dishes.

† Ber. d. ch. G., 1882, p. 1197.

‡ The most acid fractions were also pure benzoic acid, as was to be expected.

was divided into difluorbenzoic acid and benzoic acid, as proved by analyses of the barium salt. We are convinced, therefore, that no monofluorbenzoic acid is formed by the action of chromic superfluoride on benzoic acid, but the products of the reaction are only difluorbenzoic acid and chromic fluoride with a little chromic anhydride as an impurity.

Difluorbenzoic Acid, $C_6H_3F_2COOH$.

The acid prepared and purified, as described above, appears when sublimed in white flattened needles looking very much like benzoic acid, when crystallized from alcohol or benzol in short fine needles; it sublimes at a temperature far below its melting-point, 232° (uncor.), but with much more difficulty than benzoic acid, and burns with a strongly green-bordered flame. It is essentially insoluble in cold water, and only slightly soluble in hot, the boiling solution depositing a few crystalline flocks of the acid on cooling; not very freely soluble in cold alcohol or benzol, but freely in either of these solvents when hot, very soluble in ether or glacial acetic acid, less so in methyl alcohol, and almost insoluble in ligroine, or carbonic disulphide. Benzol is the best solvent for purifying it by crystallization.

Its composition was established by the following combustions: —

I. 0.2549 gr. of substance burnt with plumbic chromate in a closed tube* gave 0.4964 gr. of carbonic dioxide and 0.0982 gr. of water.

II. 0.1595 gr. gave 0.3131 gr. of carbonic dioxide and 0.0506 gr. of water.

	Calculated for $C_7H_4F_2O_2$.	Found. I.	II.
Carbon	53.16	53.13	53.52
Hydrogen	2.53	4.28	3.53

The ammonic difluorbenzoate is decomposed by evaporating its solution to dryness; but a solution freed from ammonia by boiling gave white precipitates with plumbic acetate, and mercurous, mercuric, and argentic nitrates, and a bluish white precipitate with cupric sulphate.

Baric Difluorbenzoate, $Ba(C_7H_3F_2O_2)_2$, made by boiling the acid with baric carbonate and water, crystallizes in white scales, and contains no water of crystallization even when only air-dried.

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* We found it impossible to obtain agreeing results when the combustion was performed in the ordinary way with oxygen.

I. 0.2716 gr. of the salt dried at 110° gave 0.1395 gr. of baric sulphate.

II. 0. 2674 gr. gave 0.1378 gr. of baric sulphate.

	Calculated for $Ba(C_7H_3F_2O_2)_2$.	Found. I.	II.
Barium	30.38	30.20	30.28

Its solubility in water was determined according to the method of Victor Meyer: —

I. 1.5814 gr. of a solution saturated at 15° gave 0.0188 gr. of the salt by evaporation.

II. 2.6260 gr. gave 0.0310 gr. of the salt.

Therefore, the solution saturated at 15° contains the following percentages of the salt: —

I.	II.
1.19	1.18

Calcic Difluorbenzoate, $Ca(C_7H_3F_2O_2)_2 \cdot 3\,H_2O$.

This very characteristic salt, made by boiling the acid with calcic carbonate and water, begins to crystallize out, as soon as the liquid is somewhat concentrated, in bundles of silky needles, frequently a centimeter long, and slightly branched at a very acute angle.

I. 0.7886 gr. of the air-dried salt lost 0.1058 gr. at 100°.

II. 0.3605 gr. lost 0.0495 gr.

	Calculated for $Ca(C_7H_3F_2O_2)_2 \cdot 3\,H_2O$.	Found. I.	II.
Water	13.28	13.42	13.73

I. 0.2440 gr. of the salt dried at 100° gave 0.0914 gr. of calcic sulphate.

II. 0.3024 gr. gave 0.1153 gr. of calcic sulphate.

	Calculated for $Ca(C_7H_3F_2O_2)_2$.	Found. I.	II.
Calcium	11.30	11.02	11.21

Its solubility in water was determined according to the method of Victor Meyer: —

I. 2.0134 gr. of a solution saturated at 15° gave 0.0100 gr. of the anhydrous salt by evaporation.

II. 5.1731 gr. gave 0.0256 gr. of the anhydrous salt.

Therefore, the solution saturated at 15° contains the following percentages of the anhydrous salt.

I.	II.
0.50	0.49

The calcium salt when heated with an excess of lime gives off a combustible vapor, probably difluorbenzol, as only 4 per cent of fluorine was removed from the acid in this way, but we do not intend to try to isolate this product for fear of interfering with Paterno. This observation was made in an attempt to determine the fluorine in the acid by Piria's method,* which showed that a much larger layer of alkali than could be obtained in this way was needed to remove the fluorine from the organic compound. We propose in our subsequent work to make another effort to solve this difficult problem in organic analysis.

It is to be observed that the large percentages of hydrogen obtained in the combustion of the acid correspond to the formula $C_6H_5F_2CO_2H$ better than to $C_6H_3F_2CO_2H$, and that our other analytical work is not capable of deciding between these formulas. The formula $C_6H_5F_2CO_2H$ would be that of an oxybenzoic acid containing two atoms of fluorine instead of one of oxygen $\left(C_6H_4\begin{matrix}COOH\\F_2H\end{matrix}\right)$, and although the difficulty of removing the fluorine from the acid rendered this formula highly improbable, we have thought it necessary to prove that it was incorrect. For this purpose we treated the acid with a large excess of potassic hydrate in alcoholic solution, and analyzed the potassium salt, which can be precipitated by ether in broad silvery scales, when we obtained an amount of potassium corresponding to the formula $C_6H_3F_2CO_2K$.

* H. Schiff, Ann. Chem., cxcv. 293.